Review on Applications of Nanocatalyst in Refineries and petrochemicals

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Abstract

In the nanoscience where all the devices and technologies are going to smaller in size with improved properties, catalysis is an important field of application. In recent years, nanocatalysis has become more emerging field of science due to its high activity, selectivity and productivity. In this mini-review, we are trying to summarize data reported in literature for application of nano sized catalyst in Refineries and petrochemicals industries. By decreasing the size of the catalyst, advantages such as large surface area would be exposed to the reactant. Main applications of nanocatalysts in steam reforming, bio diesel production, and several other point of application are discussed here in detail.

Keywords: Nanocatalyst, Applications, Refineries, petrochemicals

1. Introduction

Catalysis plays important role in chemical transformations and lies at the heart of countless chemical protocols, from academic research at laboratories level to the chemical industry level [1]. By using catalytic reagents, one can reduce the temperature of a transformation, reduce a waste and enhance the selectivity of a reaction that potentially avoids the unwanted side reactions leading to a green technology.

The field of nanocatalysis (the use of nanoparticles to catalyze reactions) has undergone an explosive growth during the past decade, both in homogeneous and heterogeneous catalysis. Nanocatalysts could be classified into four distinct types, namely: nanoparticulate, nanoporous, nanocrys-talline, and supramolecular catalysts. Since nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive candidates for use as catalysts. Homogeneous and heterogeneous catalysis are well-known as being two different domains defended by two scientific communities (molecular chemistry and solid state), although both are looking for the same objective, the discovery of better catalytic performance. This difference between homogeneous and heterogeneous catalysis is mainly due to the materials used as catalysts, as well as to the catalytic reaction conditions applied.

Nanocatalysts have combined advantages of both the homogeneous and heterogeneous catalytic systems. Nanocatalytic system allows the rapid, selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery. Because of nano size (high surface area) the contact between reactants and catalyst increases dramatically (this phenomenon is close to homogeneous catalysis). Insolubility in the reaction solvent makes the catalyst heterogeneous and hence can be separated out easily from the reaction mixture (this phenomenon is close to heterogeneous catalysis) [2-5].

The method of catalyst preparation plays an important role in the physical properties and catalytic performance of the catalysts [6]. For a given metal–support system, the particle size and metal–support interaction depends on the preparation method [7-9]. In general, catalysts prepared by impregnation and deposition–precipitation have weak interaction between metal and support, while those prepared by sol–gel, co-precipitation and fusion methods exhibit strong interactions [10].

A key objective of nanocatalysis research is to produce catalysts with 100% selectivity, extremely high activity, low energy consumption, and long lifetime. This can be achieved only by precisely controlling the size, shape, spatial distribution, surface composition and electronic structure. In this article, the exciting opportunities of nanocatalysis in petrochemical and refining processes, as well as the challenges in developing nanostructured catalysts for industrial applications, are discussed.

2. Concepts of nanocatalyst

Nanomaterials are those which have structured components with at least one dimension less than 100 nano-meters (10^{-9} meters). Nanoparticles of material show different properties compared to larger particles of the same material. With decreasing particle size, bulk properties are lost as the continuum of electronic states breaks down (i.e. quantum size effects) and as the fraction of surface atoms becomes large. Due to the different effects in terms of volume, quantum size, surface, and macroscopic quantum tunnel, nanometer-sized particles are expected to possess many improved properties over those of bulk and micrometer-sized particles, including catalysis. In particular importance for chemistry, surface energies and surface morphologies are also size-dependent, and this can translate to enhanced intrinsic surface reactivity [11].

To understand nanoparticles have a much greater surface area per unit mass compared with larger particles, due to the **surface area to volume ratio.** Since atoms on the surface of a material are often more reactive than those in the center, so a larger surface area means the material is more reactive [12]. Figure 1 shows this idea; the cube on the left has the same volume as the smaller cubes added together on the right. However, the total surface area is much larger for the smaller cubes.

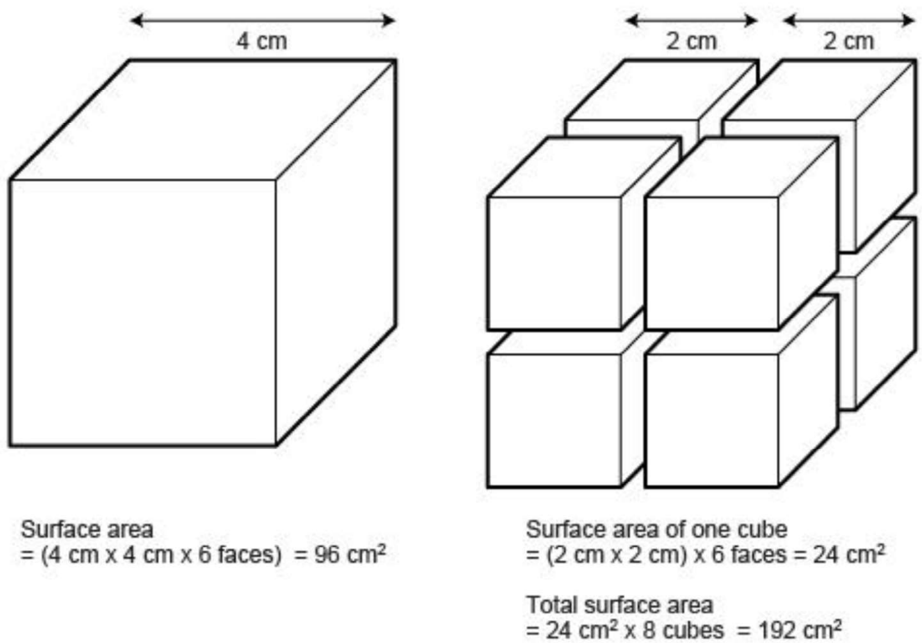

Fig (1) Nanoparticles have more surface area to volume than larger particles

3. Nanocatalyst; effect of size reduction

In view of the numerous potential benefits that can accrue through their use as shown in Figure 2, nanostructured catalysts have been the subject of considerable research attention in recent times. Many applications and patents have also been realized adopting such nanostructured catalysts leading to significant process improvements as exemplified below [13].

i. production of high value products with inexpensive raw materials,
ii. energy-efficient and environmentally-benign chemical conversion processes,

iii. increasingly stringent environmental regulations,

iv. Increased selectivity, activity and lifetime of catalysts by controlling pore size and particle characteristics

v. Replacement of precious metal catalysts by catalysts tailored at the nanoscale and use of base metals, thus improving chemical reactivity and reducing process costs [14].

vi. Catalytic membranes by design that can remove unwanted molecules from gases or liquids by controlling the pore size and membrane characteristics.

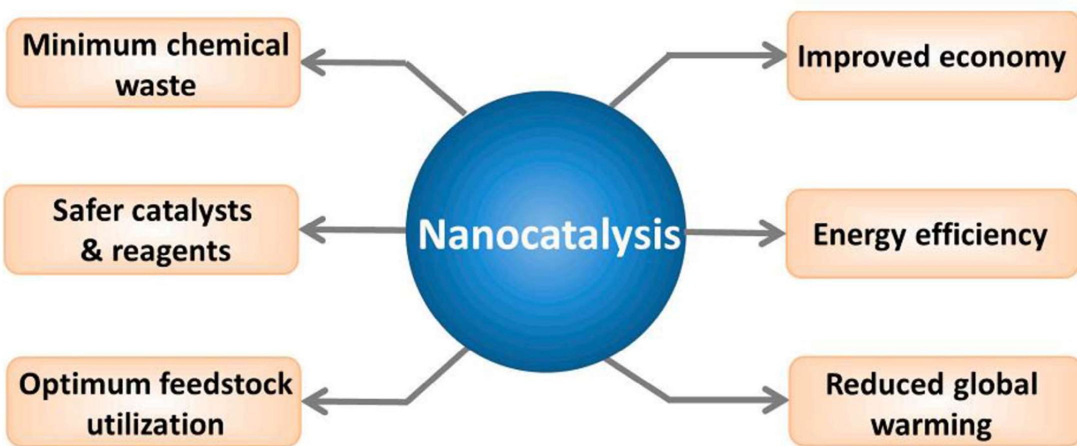

Fig. (2) Benefits of nanocatalysis

4. Application of nanocatalyst in refineries and petrochemicals

In view of the numerous potential benefits, nanocatalysts have been applied in various areas, including refineries [15], the pharmaceutical industry [16], the chemical industry [17], food processing [18], and environmental applications [19]. In this section we are trying to collect some literature data for refineries and petrochemical applications of nanocatalyst reported within the last few years.

4.1. Gasoline steam reforming

Hydrogen is the latest in the succession of energy providers, with many social, economic, and environmental benefits to its credit including its utilization in chemical industries which accounts for 40% of its consumption. This implicates the preciousness of H_2 and its high demand to the world today and tomorrow. Nowadays, the automotive industry pays great attention to catalytic reforming of gasoline (CRG) to produce hydrogen, owing to the existing infrastructure and high power density of gasoline. This hydrogen can be trans-formed cleanly and efficiently into electricity using fuel cells. CRG has two advantages when used as fuel: first, the higher energy efficiency with respect to the use of internal combustion engine. Second, it has an environmental impact by eliminating the pollutant emissions.

The main catalytic reactions for hydrogen production from petroleum fuels are steam reforming, partial oxidation, and auto-thermal reforming [20]. Among those methods, catalytic steam reforming (CSRG) shows the highest conversion to H_2 [21]. In order to achieve high H_2 selectivity on a metallic catalyst for the CSRG, the catalysts should have a high C–C bond breaking rate and a low methanation reaction rate. According to the literature [22, 23] Ni is a potential catalyst for the steam reforming reactions because it has high rate of C–C bond breakage, good water gas shift activity, and moderate methanation reaction capacity.

However, supported Ni catalysts have some problems such as Ni particle sintering and coke deposition, resulting in catalyst deactivation [24]. Therefore, it is necessary to develop catalysts, it has been reported that Ni catalyst supported on nano-particles of ZrO2 could be highly active and stable for CRM [25]. It is also reported that nano-sized Ni–Ce–ZrO2 catalyst could be active and stable in CRM [26]. High specific surface area, homogeneous dispersion of metals, design of meso-pore structure, control of metal– support interaction, and also preparation of catalysts in nano-form are important factors showing better catalytic activity and stability in steam reforming reaction [27]. Nano-sized catalysts are prepared either by impregnation or co-precipitation of metal with the support [28].

4.2. Bio diesel production

With the increase of environment protection consciousness and decrease of petroleum reserves, biodiesel, defined as the monoalkyl esters of fatty acids, has been the focus of a considerable amount of recent research as an alternative renewable fuel. More and more biodiesel is being used in many countries such as Germany, France, Italy, USA, Japan and so on [29]. The general method for the preparation of biodiesel is trans esterification reaction of oil and alcohol with homogeneous catalyst [30]. However, the homogeneous catalyst has many shortcomings, such as the difficulty in product isolation, requirement of large quantity of water and environ-mental pollution by the liquid wastes [31, 32]. A new trend in the preparation of biodiesel is to use ‘‘green’’ method based on heterogeneous catalyst [33, 34]. Despite the solid phase catalytic methods being intensively studied, the industrial applications are limited. This fact suggests that further research is necessary to solve current problems. Heterogeneous catalytic methods are usually mass transfer resistant, time consuming and inefficient [35]. Nanocatalysts have high specific surface and high catalysis activities, may solve the above problems. Wen etal. (2010) [36] studied that the solid base nanocatalyst KF/CaO can be used for bio-diesel production with yield of more than 96%. The catalyst is well used to convert the oil with higher acid value into bio-diesel. It is porous with particle sizes of 30–100 nm. XRD analysis showed the catalyst has new crystal $KCaF_3$, which increases catalytic activity and stability. The high specific surface area and large pore size are favorable for contact between catalyst and substrates, which effectively improved efficiency of transesterification.

4.3. Fuel cell

One of the most important challenges for the ultimate commercialization of fuel cells is the preparation of active, robust, and low-cost catalysts. The basic function of the catalyst layer present in a fuel cell is to provide a conductive environment for electrochemical reactions. The main processes that occur in the catalyst layer include mass transport, interfacial reactions at electrochemically active sites, proton transport in the electrolyte phase, and electron conduction in the electronic phase. The oxidation reaction occurs in the anode catalyst layer, while oxygen reduction occurs in the cathode catalyst layer. Anodic and cathodic reactions require metallic active sites to break molecular bonds of gaseous diatomic reactants. The oxidation reaction possesses a lower over-potential and higher rate than oxygen reduction; thus, oxygen reduction is a significant source of voltage loss [37].

Literature data show that Platinum (Pt) based binary catalysts per-form better as catalysts for oxygen reduction than pure Pt. However, Pt catalysts suffer from several drawbacks including slow kinetics, low efficiency, high cost, and limited lifetime. Thus, current research is focused on the development of catalyst materials with low cost, high performance, high stability, and durability. Nanoscience has stimulated extensive interest in nanostructured catalysts to significantly improve these feachres. In particular, the use of nanocatalysis in fuel cells can significantly improve the electrocatalytic performance for high energy density and high power density, while reducing the manufacturing cost. The prominent electrocatalytic behavior of the nanomaterials mainly derives from their unique physical-chemical properties such as size, shape, pore structure/distribution, surface defects [38, 39].

4.4. Alcohol oxidation

Methanol and ethanol are the most studied alcohols for Direct Alcohol Fuel Cell (DAFC) application [40]. Use of ethanol as fuel in DAFCs provides many advantages over methanol due to its renewability, low toxicity, safety, high energy density, and its easy production in great quantities from biomass [41].

Pt has been demonstrated as the only active and stable noble metal for alcohol oxidation, particularly in acid medium. However, it is well known that pure platinum is readily poisoned by CO-like intermediates of methanol or ethanol electro-oxidation (42). On the other hand, the high cost of the platinum limits its use. One approach to cost reduction is to use the Pt-based alloys to reduce the Pt loading. Another effective approach is to increase the utilization efficiency of Pt electrocatalysts by exploring the high surface area supports such as high surface area carbon.

Kadirgan et al. (2009) [43] investigated the effect of Pt–Pd/C nano-sized electrocatalysts on oxidation of alcohols. The experiments confirm that Pt–Pd/C nano-particles synthesized lead to synergistic effect toward methanol and ethanol oxidation. Also it is an enhancement of the reaction kinetic for both alcohols was observed increasing the working temperature.

4.5. Waste water treatment

Halogenated organic compounds (HOCs) are among the most widely distributed water pollutants in industrialized countries. HOCs are mostly hazardous and toxic compounds which have very often a high persistence and may cause serious health problems such as cancer or mutagenic damage. Therefore, a complete destruction of these compounds is aspired or even mandatory.

Ordinary wastewater treatment works cannot handle the problem. Thus, high priced and energy-intensive methods still have to be employed to solve this problem. Common practice to dispose of industrial wastewaters contaminated with threshold load of organic solvents and only traces of HOCs is incineration. However, the incineration of aqueous waste is a waste of energy, and also organic compounds such as alcohols could be removed by bacterial treatment in a wastewater treatment plant. Current detoxification techniques such as adsorption on activated carbon or oxidation of the wastewater components do not lead to an environmentally friendly and economically priced solution. Hildebrand et al. (2008) [44] suggested an idea to detoxify the water by a selective destruction of the HOCs using the palladium (Pd) nanocatalysts. Detoxification means that persistent HOCs are converted into organic compounds which can easily be removed by biodegradation in a wastewater treatment plant.

Nano-sized Pd catalysts have been successfully tested for selective hydrodehalogenation of wastewater pollutants at the laboratory scale. Dehalogenation using Pd on nano-scale supports shows the true inherent activity of Pd clusters which is several orders of magnitude higher than reached in fixed-bed arrangements due to minimized mass-transfer limitations.

5. Conclusion

Today it is very promising that scientists are able to solve current environmental, social and industrial problems. Nanoparticles have a large surface area to volume ratio compared to bulk materials, they are attractive to use as catalysts. This review provide the basis of understanding of nano-size effects on catalytic behavior such as enhanced catalyst activity, great surface area per unit mass, improving chemical reactivity and reducing process costs. The examples presented in this brief overview show how nanocatalysis can be applied to different reactions in refineries and petrochemicals.

Research in nanotechnology and nanoscience is expected to have a great impact on the development of new catalysts. The detailed understanding of chemistry of nanostructures and the ability to control materials on the nanometer scale will ensure a rational and cost efficient development of new and more capable catalysts for a chemical process.

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